AFRL-MN-EG-TP-2006-7403

INFRARED SPECTROSCOPY OF HYDROGEN CYANIDE IN SOLID PARAHYDROGEN (BRIEFING CHARTS)

C. Michael Lindsay,
National Research Council, Post Doctoral Research Associate
Mario E. Fajardo
Air Force Research Laboratory
Munitions Directorate
AFRL/MNME
Eglin AFB, FL 32542-6810

JULY 2006

CONFERENCE PAPER

AIR FORCE RESEARCH LABORATORY, MUNITIONS DIRECTORATE

■ **Air Force Materiel Command** ■ **United States Air Force** ■ **Eglin Air Force Base**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE		3. DATES COVERED *(From - To)*
	Conference Paper		

4. TITLE AND SUBTITLE
Infrared Spectroscopy of Hydrogen Cyanide In Solid Parahydrogen (BRIEFING CHARTS)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Mario E. Fajardo

C. Michael Lindsay (National Research Council, Post Doctoral Research Associate) assigned to the Air Force Research Laboratory, Munitions Directorate, AFRL/MNME

5d. PROJECT NUMBER
2502

5e. TASK NUMBER
10

5f. WORK UNIT NUMBER
15

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory,
Munitions Directorate
AFRL/MNME
Eglin AFB, FL 32542-6810

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-MN-EG-TP-2006-7403

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Same as Block 7

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL-MN-EG

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
Same as Block 8

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION A: Approved for public release; distribution unlimited.
Approval Confirmation #AAC/PA 06-02-06-271

13. SUPPLEMENTARY NOTES   This paper will be presented at the 61st Ohio State University International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, 19-23 June 2006. One of the authors is a U.S. Government employee working within the scope of his position; therefore, the U.S. Government is joint owner of the work. This paper will be published in the proceedings and the publisher may assert copyright. If so, the Government has the right to copy, distribute, and use the work. Any other form of use is ubject to copyright restrictions.

14. ABSTRACT

 Solid parahydrogen features:
 - Weak intermolecular interactions
 - Slow relaxation timescales
 - Quantum crystal: self-annealing via tunneling
 - Homogeneous environment
 - Large intermolecular distance, 3.78 Å

Parahydrogen as a matrix:
 - Very small matrix shifts, predictable (-0.5 %)
 - Nearly free rotation for small molecules
 - High impurity mobility
 - Narrow spectral linewidths (<100 MHz possible)
 - Dopants induce infrared activity in matrix

15. SUBJECT TERMS
Solid Parahydrogen, Hydrogen Cyanide, Infrared Spectroscopy

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Mario E. Fajardo
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	20	**19b. TELEPHONE NUMBER** *(include area code)*
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED			

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Infrared Spectroscopy Of Hydrogen Cyanide In Solid Parahydrogen

Dr. C. Michael Lindsay
& Dr. Mario E. Fajardo
AFRL/MNME

Infrared Spectroscopy Of Hydrogen Cyanide In Solid Parahydrogen

C. Michael Lindsay and Mario E. Fajardo

AFRL/MNME, Energetic Materials Branch, Ordnance Division, U.S. Air Force Research Laboratory, 2306 Perimeter Rd, Eglin AFB, FL 32542-5910 c.michael.lindsay@eglin.af.mil

Solid parahydrogen

Solid parahydrogen features:

• Weak intermolecular interactions

• Slow relaxation timescales

• Quantum crystal: self-annealing via tunneling

• Homogeneous environment

• Large intermolecular distance, 3.78 Å

Methane in solid p-H_2

○ p-H_2
● nearest neighbor p-H_2
● methane
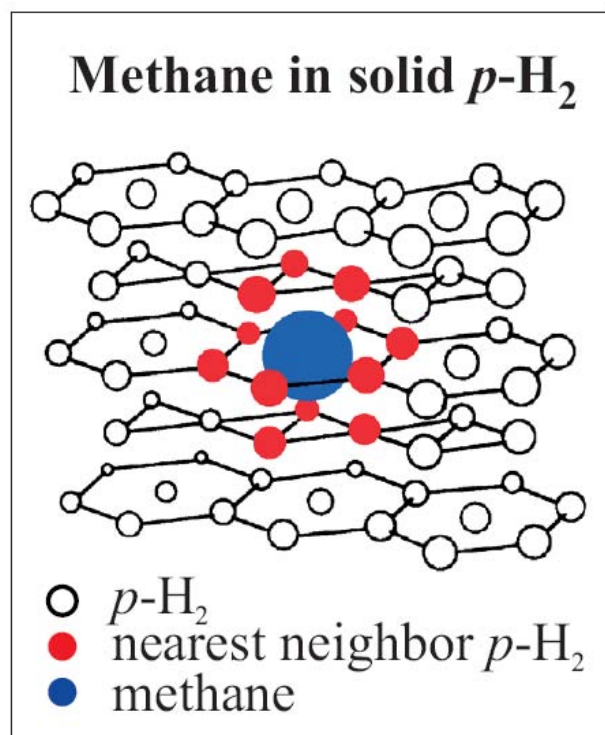
Parahydrogen as a matrix:

• Very small matrix shifts, predictable (-0.5 %)

• Nearly free rotation for small molecules

• High impurity mobility

• Narrow spectral linewidths (<100 MHz possible)

• Dopants induce infrared activity in matrix

Rotation of Molecules in Solid Parahydrogen

Rotating Dopants
- H_2O
- HCl
- N_2
- NO
- NH_3
- CH_4
- CO
- …

?

Non-rotating dopants

B_{matrix} / B_{gas}

Gas Phase Rotational Constant (cm^{-1})
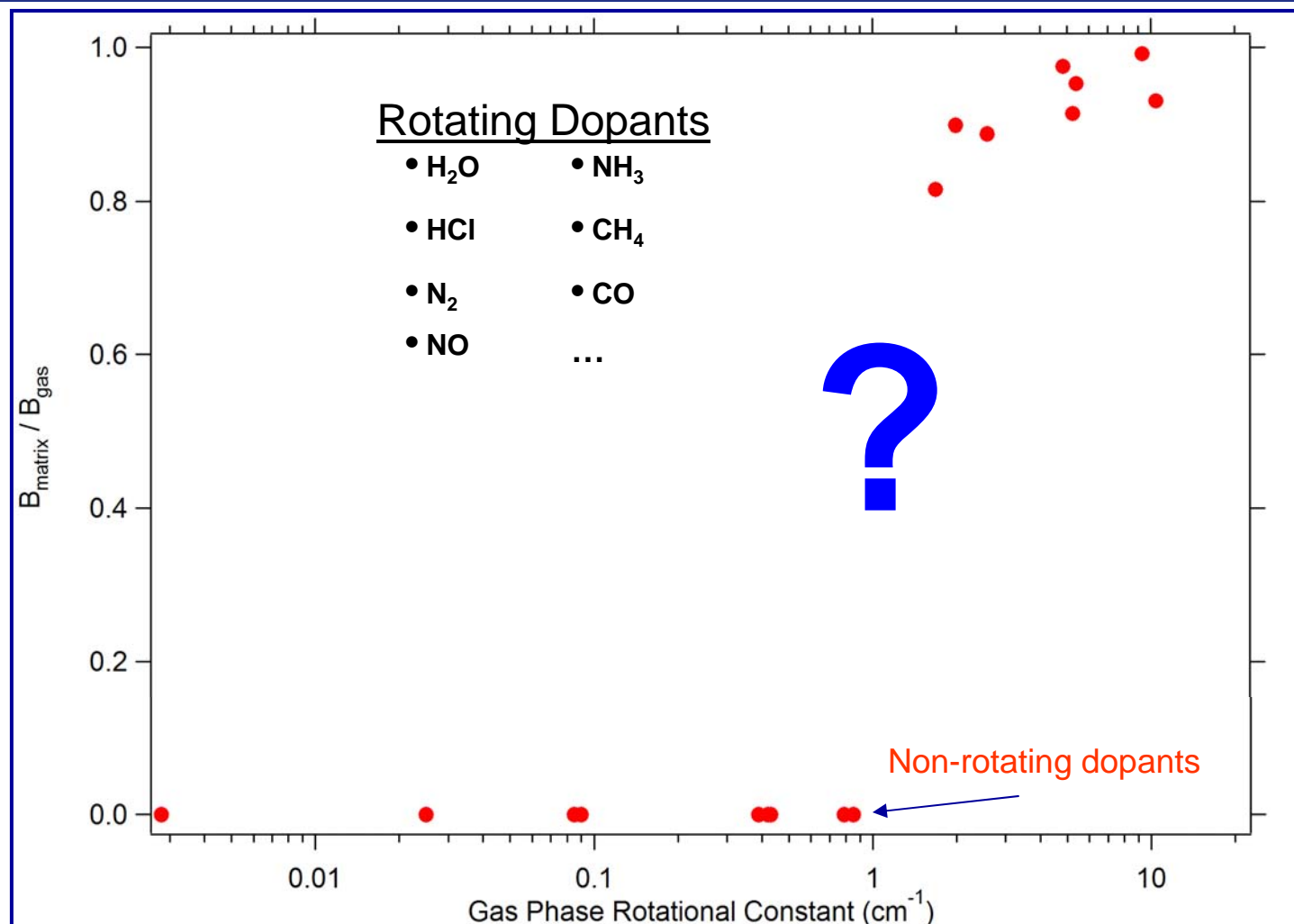
Data from the groups of M. E. Fajardo, Y.-P. Lee, and T. Momose (1995-2006).

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH

Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

4

Why study HCN?

HCN:
- $B_{gas} = 1.5$ cm^{-1}
- Large dipole: $\mu = 2.9$ Debye
- Thoroughly studied in He droplets
- H$_2$-HCN investigated theoretically

*
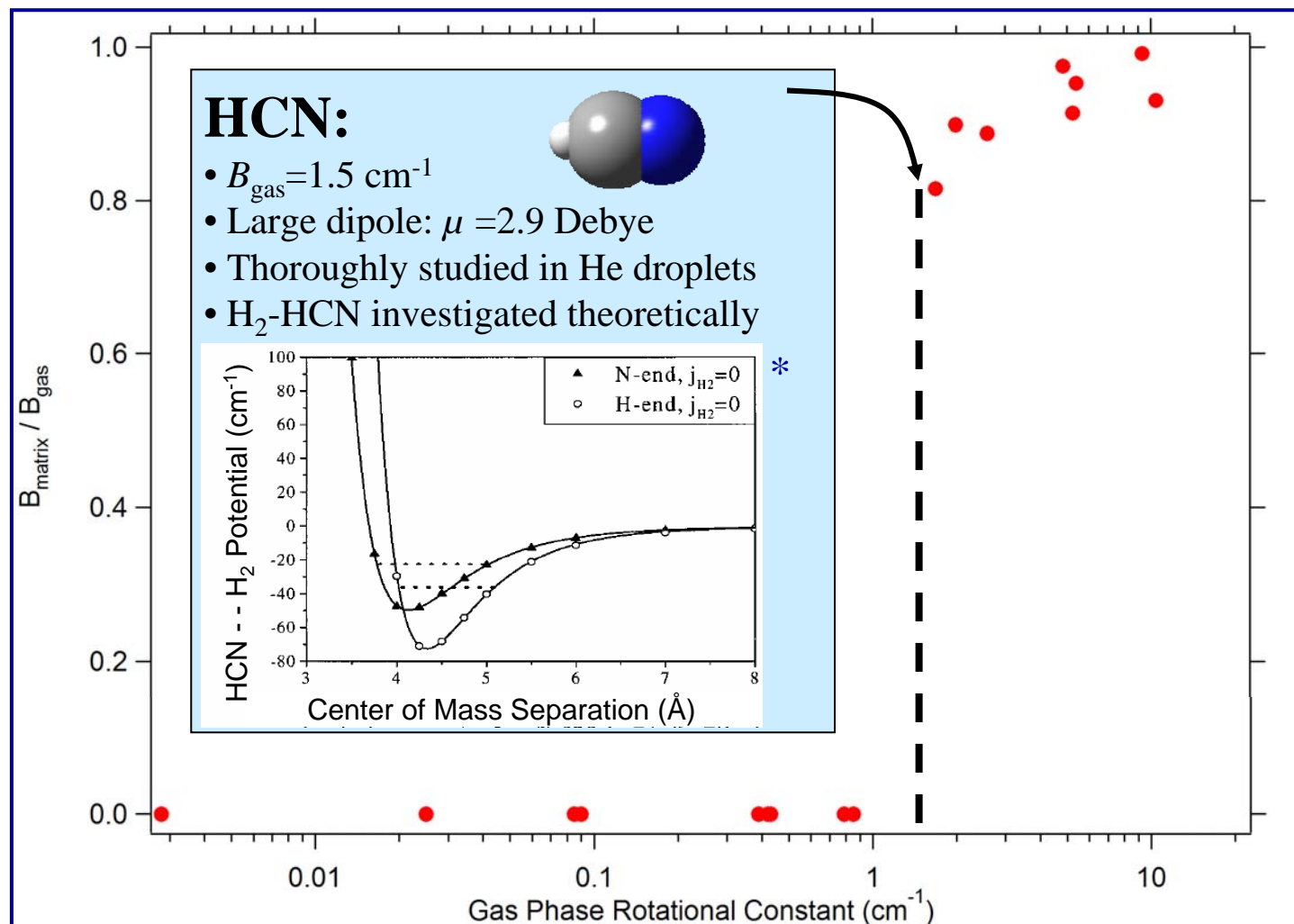
D. T. Moore, M. Ishiguro, and R. E. Miller, JCP 115, 5144 (2001)

H$_2$-HCN Potential

H$_2$-H$_2$ separation in HCP parahydrogen

N-end, j$_{H2}$=0
H-end, j$_{H2}$=0

HCN - - H$_2$ Potential (cm^{-1})

Center of Mass Separation (Å)
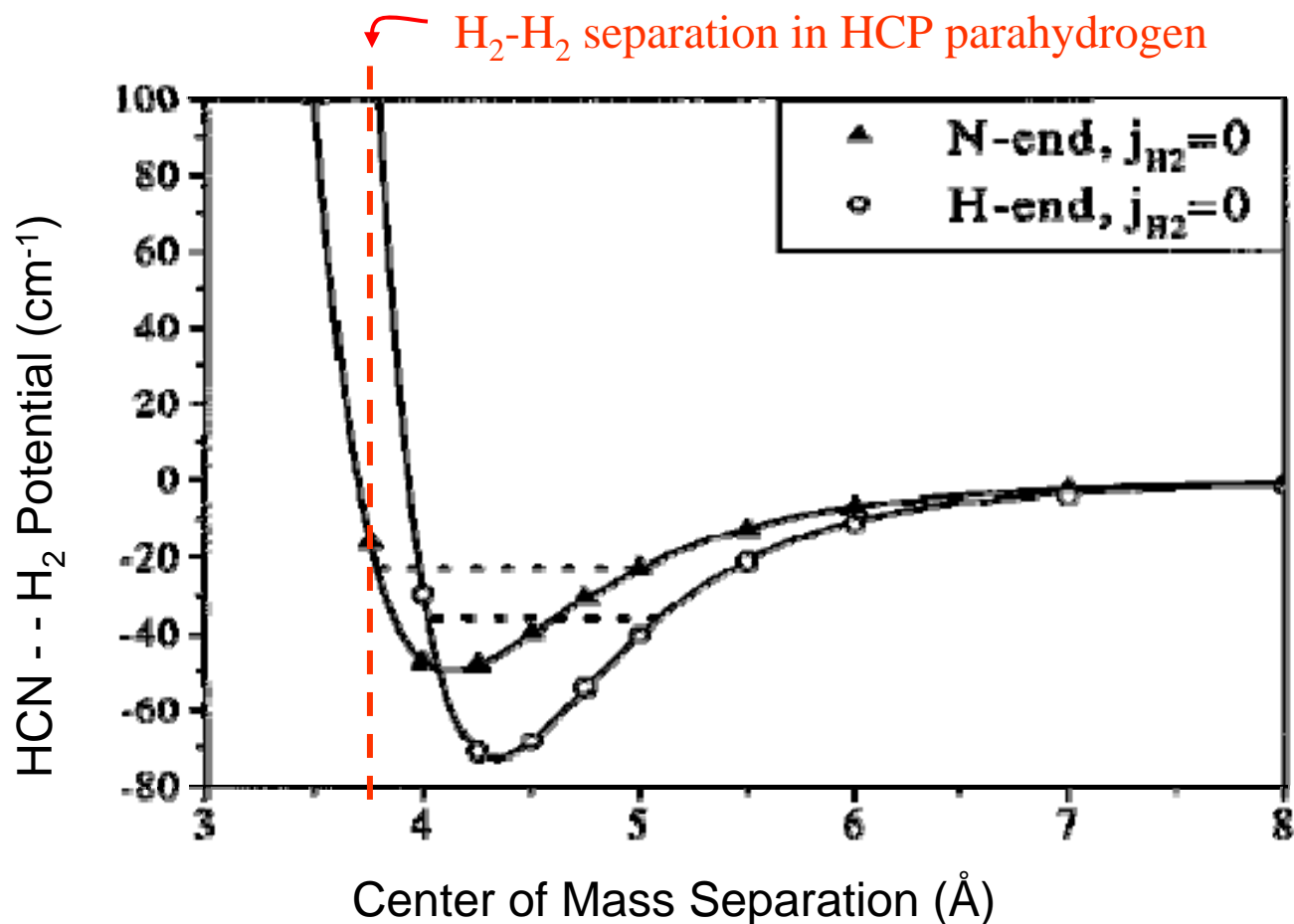
If solid parahydrogen behaved classically, the HCN will not rotate…

CCSD(T)/aug-cc-pVTZ calculations D. T. Moore, M. Ishiguro, and R. E. Miller, JCP 115, 5144 (2001)

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH
Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

6

Rapid vapor deposition of *p*-H$_2$
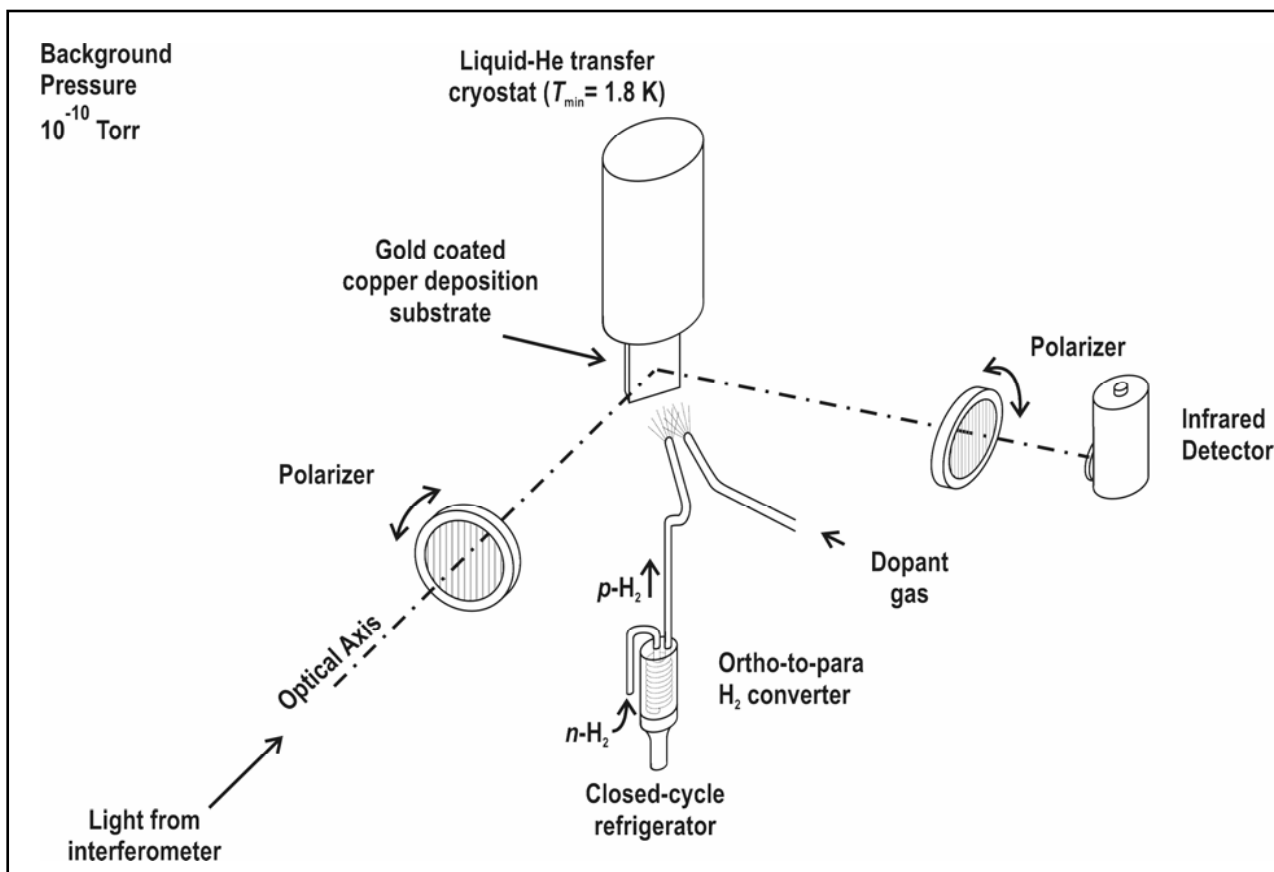
- Reflection based set-up (FTIR)
- [*o*-H$_2$] < 100 ppm
- *p*-H$_2$ deposition rate ~150 mmol/hr $\rightarrow$ ~1 mm/hr thickness
- Deposition at 2.3 K. Sample annealed at 4.3 K for 30 min.

Spectrum of annealed solid *p*-H$_2$ with and without HCN

p-H$_2$ (~100 ppm *o*-H$_2$)

× H$_2$O impurity

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH

8

Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

Spectrum of annealed solid *p*-H₂ with and without HCN

HCN ν_1 region

- Significantly more structure present than expected from spectra of gas phase molecule or non-rotating dopants.

- Expected isotopic structure is present.

- Shift ~ -9 cm^{-1}

Is HCN Rotating?

4 ppm HCN in p-H$_{2(s)}$ @ 2.3 K

Simulation, Gas Phase HCN @ 2.3 K

$*$ H^{13}CN
$\times$ HC^{15}N

Absorbance

Wavenumber (cm^{-1})

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH

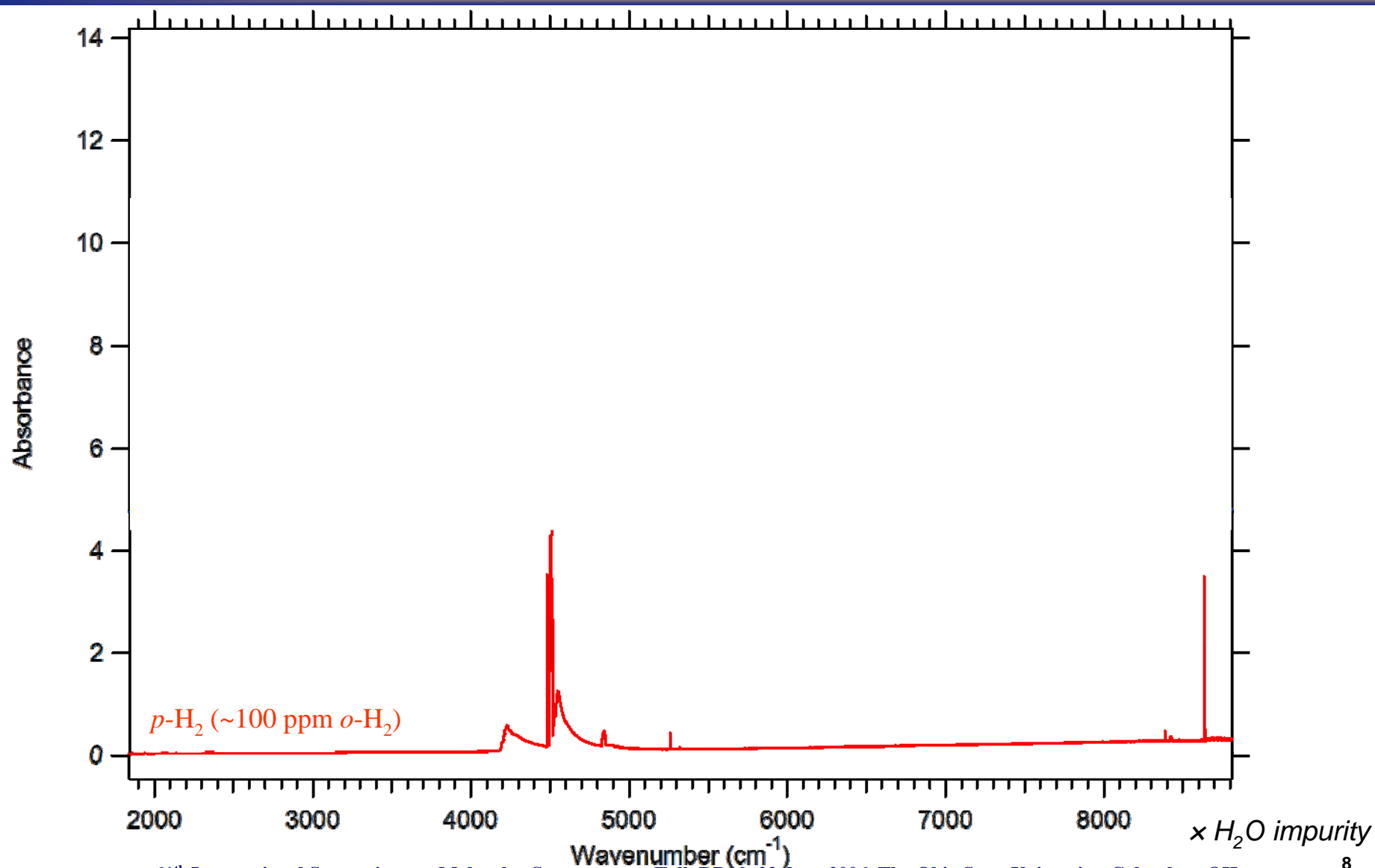Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

10

Assignment tools

Temperature Dependence
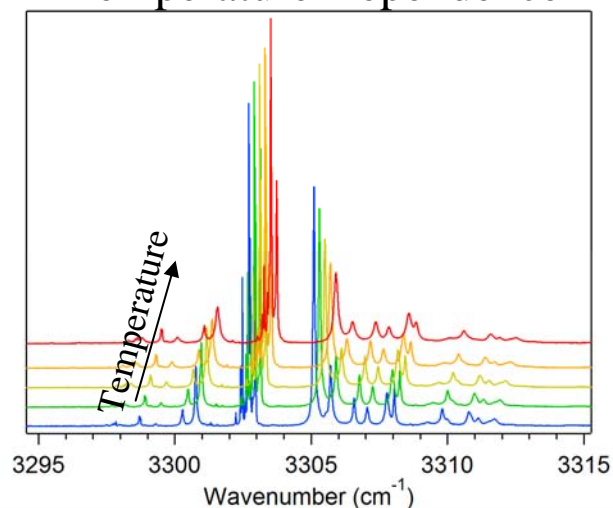
Orthohydrogen Dependence
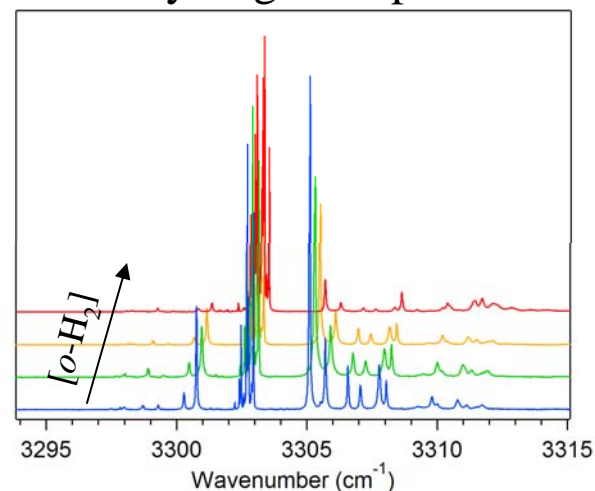
Combination Differences
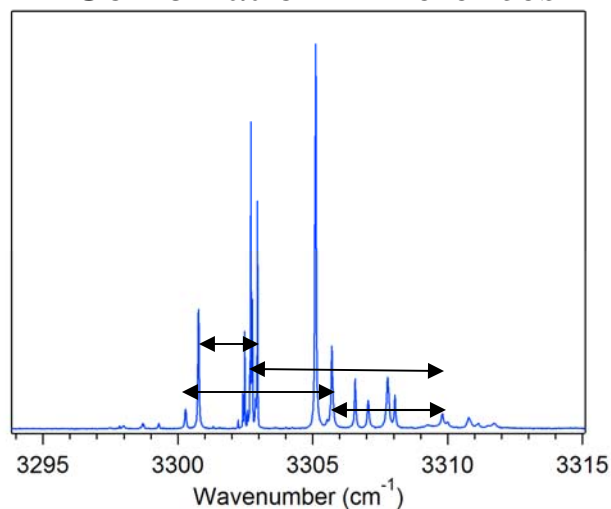
Spectrum was interpreted by its:

- **Temperature dependence**

- **Orthohydrogen concentration dependence**

- **Transition frequency combination differences**
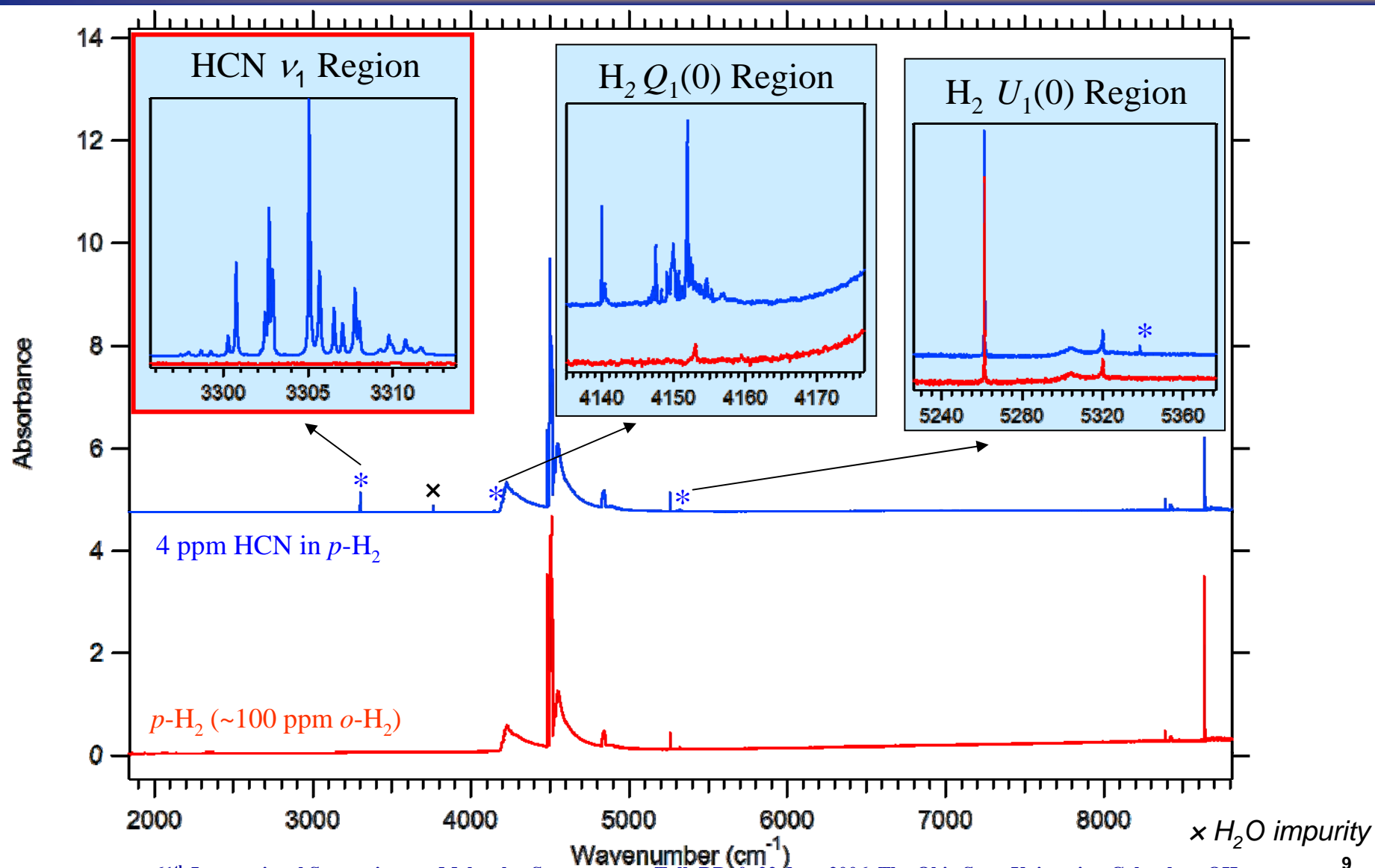
- **Polarization dependence!**

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH
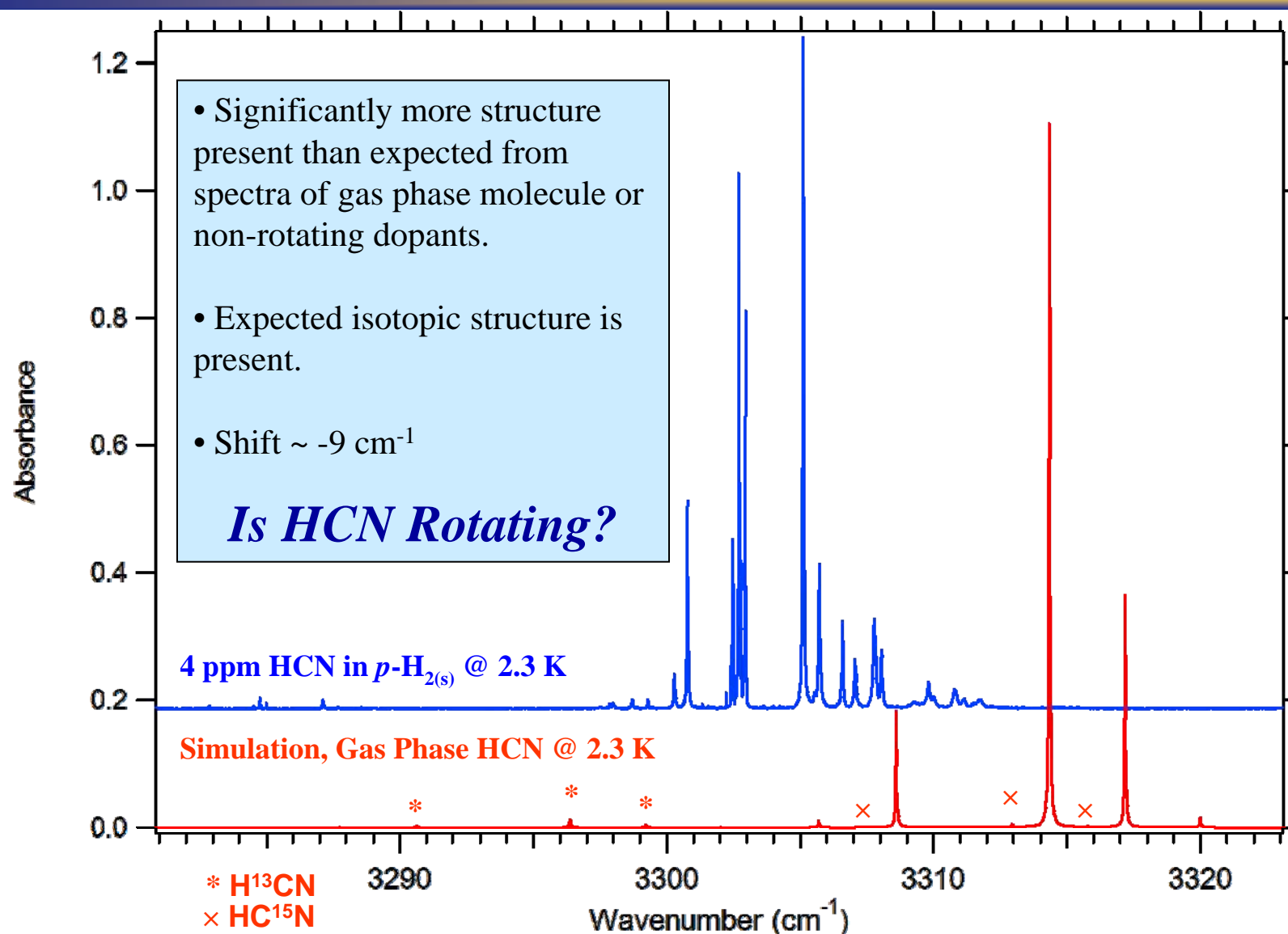**Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271**

11

Polarization spectroscopy

Annealed, 8 ppm HCN in p-H$_2$ @ 2.3 K

HCP c-axis ??

p-H$_2$

gold substrate
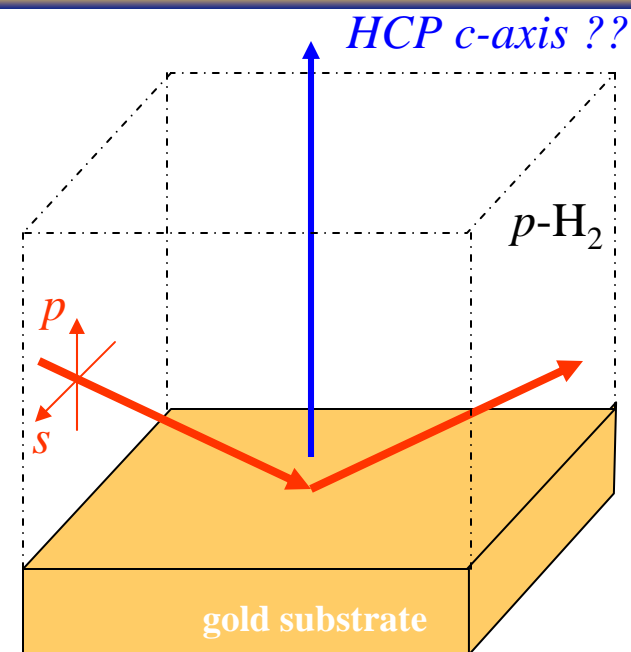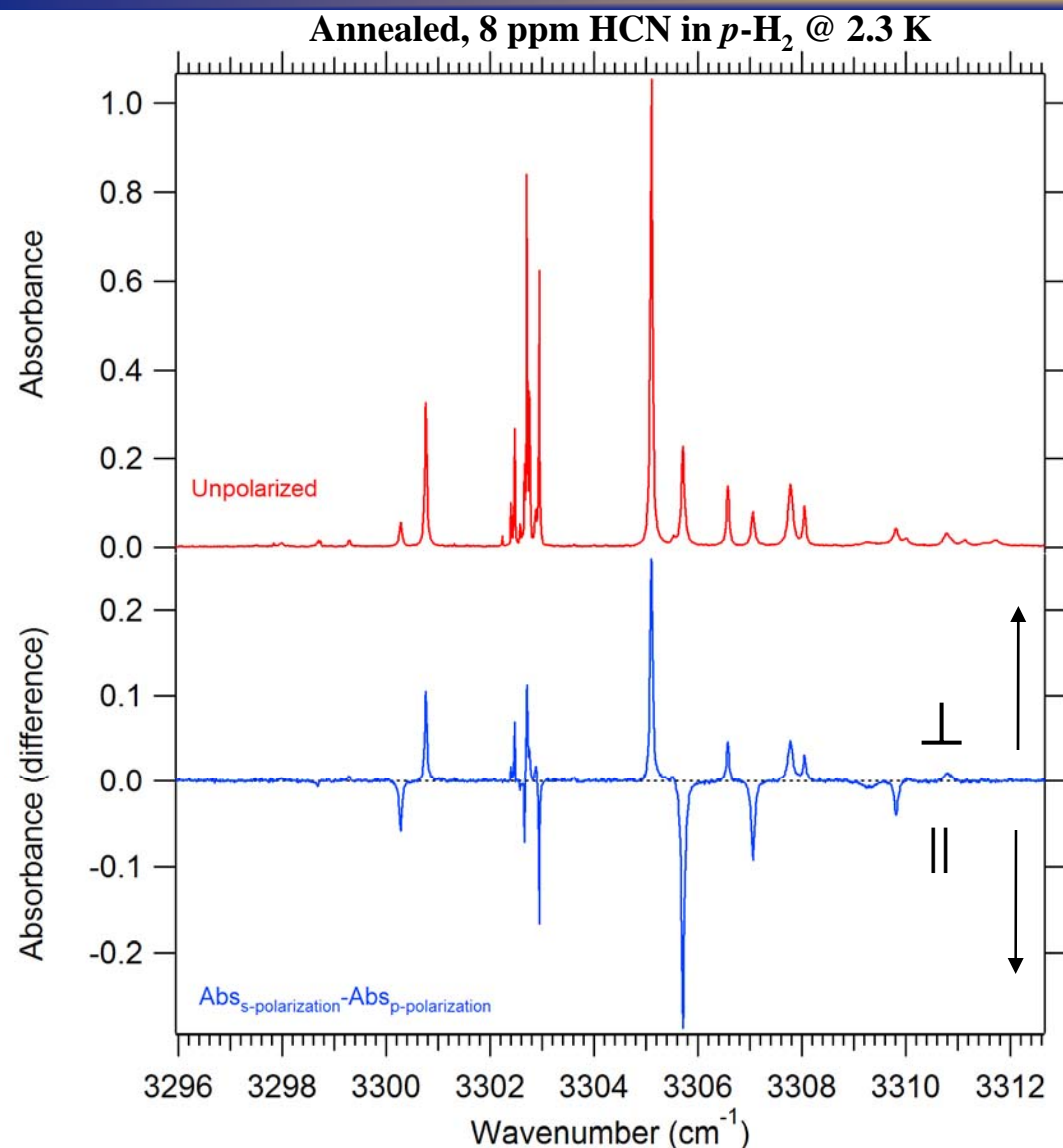
Polarization analysis provides:

- An assignment of the perpendicular and parallel components to the crystal field perturbed rotational structure (*i.e.* Δm)

- $Abs_{s\text{-}pol} - Abs_{p\text{-}pol} = \tfrac{1}{2}\,\mu^2_{\perp} - \tfrac{1}{2}\,\mu^2_{\parallel}$

- A measures of the fraction of HCP lattice with c-axis normal to substrate:

An aside… new insights into annealing mechanism in *p*-H$_2$

As-deposited, 8 ppm HCN in *p*-H$_2$ @ 2.3 K

<5 % orientation

Annealed, 8 ppm HCN in *p*-H$_2$ @ 2.3 K

80 % orientation
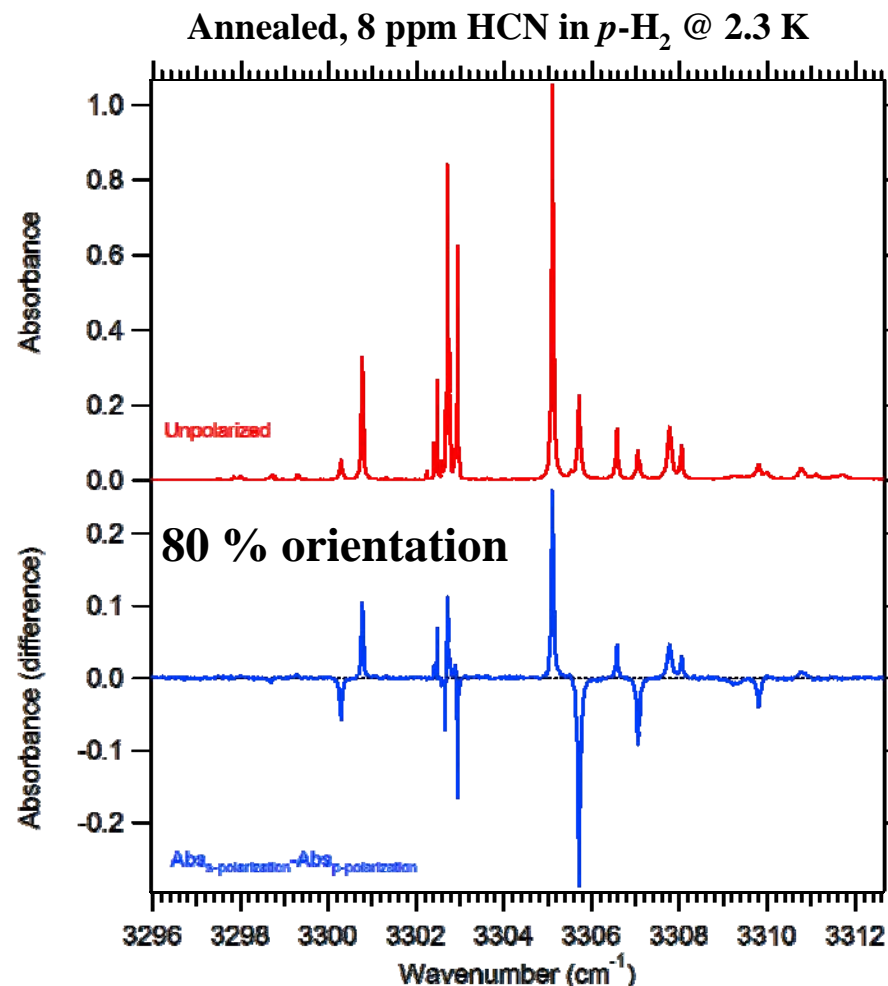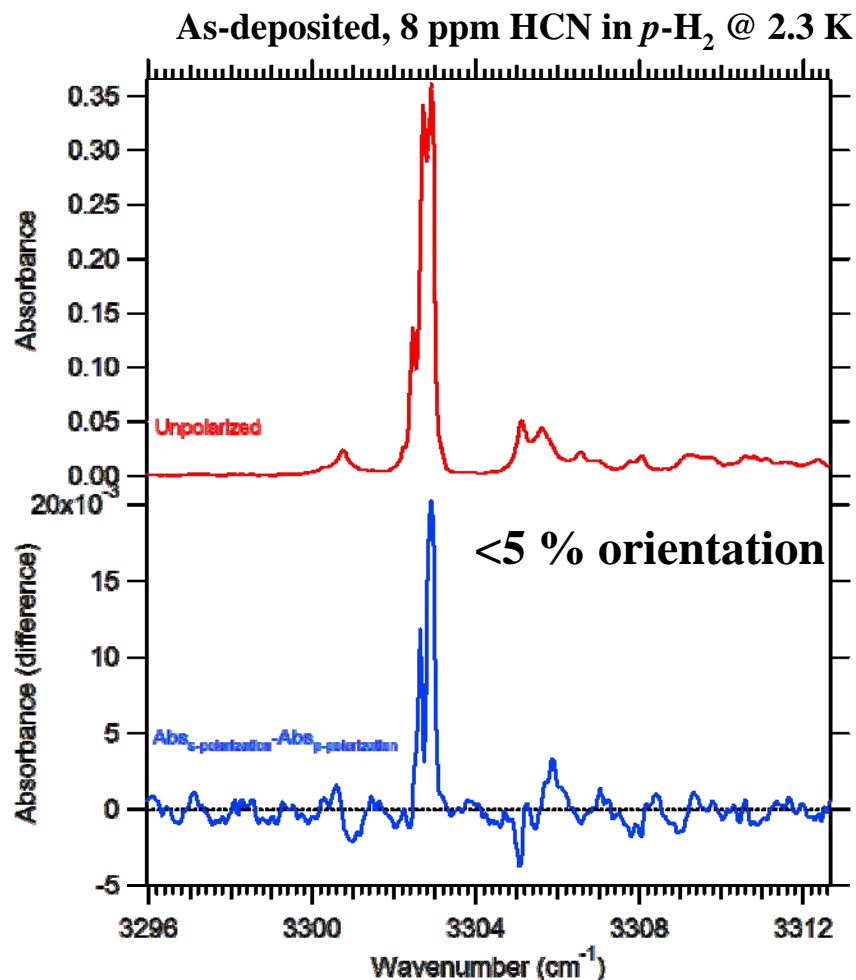
- Before annealing, less than 5% of the HCP features are oriented normal to the substrate.
- *After annealing*, ~80% of the HCP features are oriented normal to substrate!!
  → Upon deposition, HCP lattices randomly oriented, but upon annealing gain a macroscopic orientation to the laboratory frame.

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH
Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

13

Interpretation of the fine structure

Is HCN Rotating?
Yes, but only when there are no o-H$_2$ around…

HCN-pH$_2$

HCN-oH$_2$

* non-rotating (o-H$_2$)$_n$-HCN
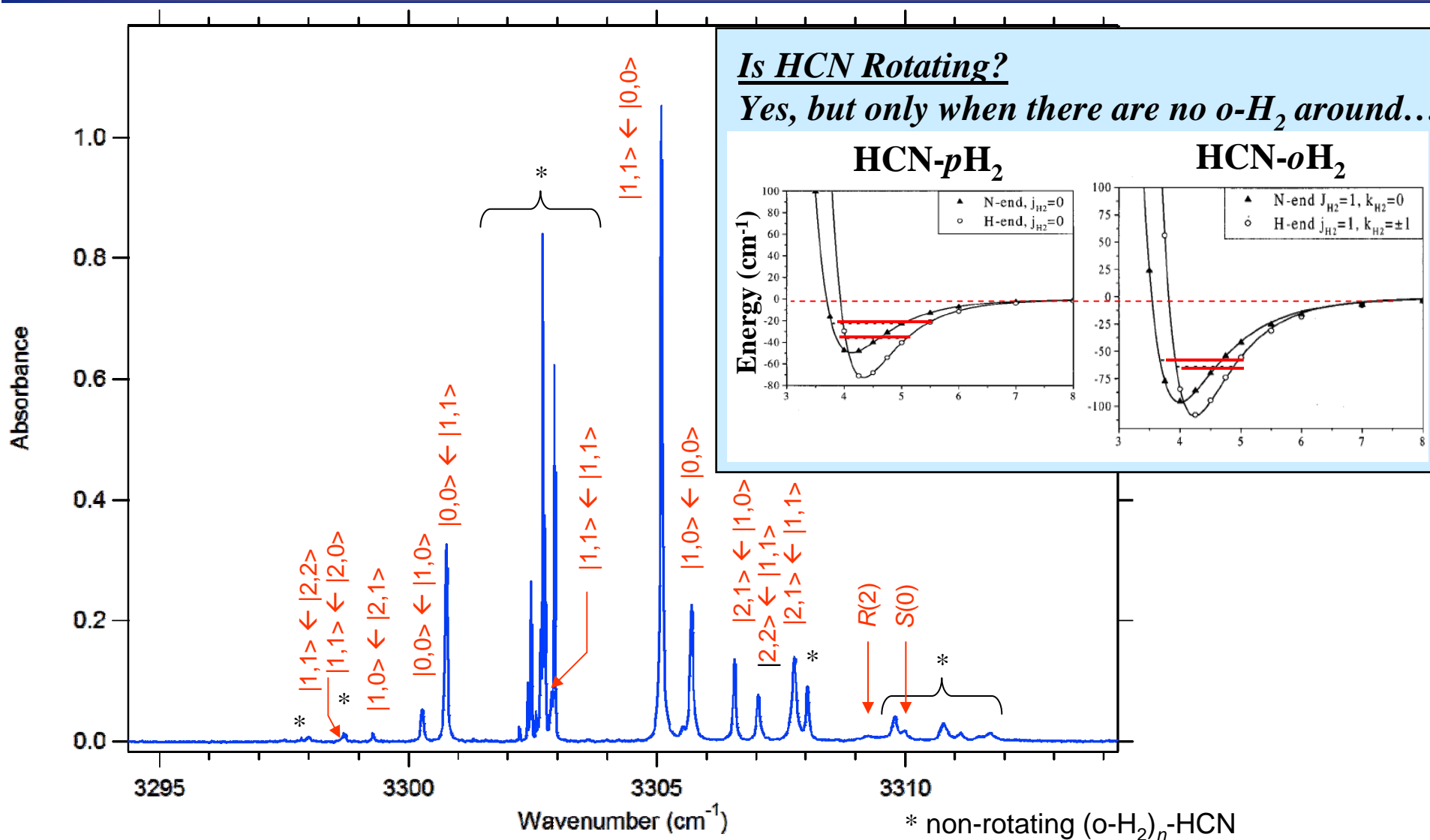
Interpretation of the fine structure in the HCN ν_1 fundamental region

- All peaks assigned!

- Each transition fit to a Lorentzian profile. Standard deviation of the fit for the last digits is shown in parentheses.

- Polarization dependence was not as clear for the higher order clusters.

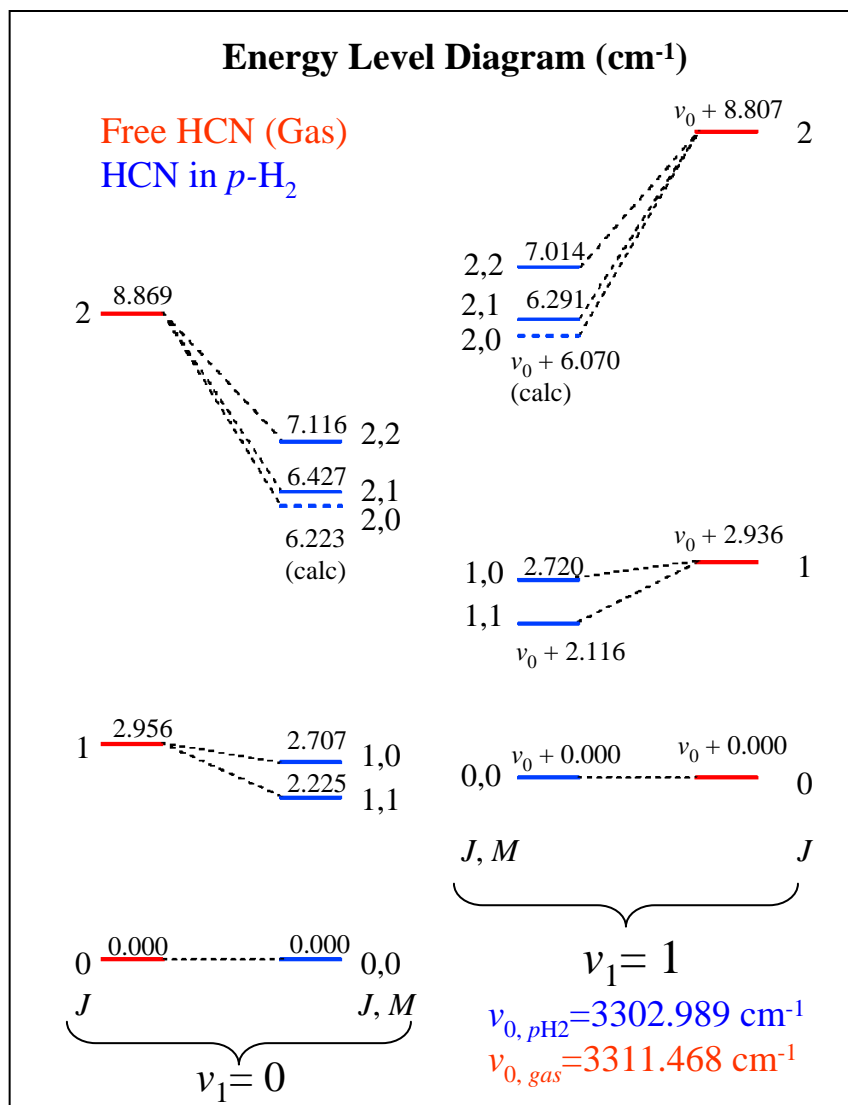| Species	$\lvert J',M'\rangle \leftarrow \lvert J'',M''\rangle$	Polarization	ν_0
HCN	$\lvert 1,1\rangle \leftarrow \lvert 2,2\rangle$	$\perp$	3297.989(5)
HCN	$\lvert 1,1\rangle \leftarrow \lvert 2,1\rangle$	$\parallel$	3298.678(3)
HCN	$\lvert 1,0\rangle \leftarrow \lvert 2,1\rangle$	$\perp$	3299.285(10)
HCN	$\lvert 0,0\rangle \leftarrow \lvert 1,0\rangle$	$\parallel$	3300.282(1)
HCN	$\lvert 0,0\rangle \leftarrow \lvert 1,1\rangle$	$\perp$	3300.764(1)
HCN	$\lvert 1,1\rangle \leftarrow \lvert 1,1\rangle$	$\perp$	3302.880(1)
HCN	$\lvert 1,1\rangle \leftarrow \lvert 0,0\rangle$	$\perp$	3305.105(1)
HCN	satellite	$\perp$	3305.530(2)
HCN	$\lvert 1,0\rangle \leftarrow \lvert 0,0\rangle$	$\parallel$	3305.709(1)
HCN	$\lvert 2,1\rangle \leftarrow \lvert 1,0\rangle$	$\perp$	3306.572(1)
HCN	$\lvert 2,1\rangle \leftarrow \lvert 1,1\rangle$	$\parallel$	3307.055(1)
HCN	$\lvert 2,2\rangle \leftarrow \lvert 1,1\rangle$	$\perp$	3307.778(1)
HCN	R(2)?	$\parallel$	3309.328(16)
HCN	$\lvert 2,2\rangle \leftarrow \lvert 0,0\rangle$	$\perp$	3310.001(5)
HCN-oH2 (ip)	in-plane cluster	$\perp$	3302.708(1)
HCN-oH2 (op)	out-of-plane cluster	$\parallel$	3302.946(1)
oH2-HCN (ip)	in-plane custer	$\perp$	3308.046(1)
oH2-HCN (op)	out-of-plane cluster	$\parallel$	3309.803(1)
(oH2)n-HCN			3302.238(1)
(oH2)n-HCN			3302.405(1)
(oH2)n-HCN			3302.474(1)
(oH2)n-HCN			3302.579(1)
(oH2)n-HCN			3302.663(1)
(oH2)n-HCN			3302.760(1)
(oH2)n-HCN			3310.775(7)
(oH2)n-HCN			3310.859(25)
(oH2)n-HCN			3311.128(5)
(oH2)n-HCN			3311.479(12)
(oH2)n-HCN			3311.717(9)
(HCN)n			3297.771(11)
(HCN)n			3297.844(4)
(HCN)n			3298.697(4)
(HCN)n			3298.739(4)

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH

Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

15

Interpretation of the fine structure

Energy Level Diagram (cm⁻¹)

Free HCN (Gas)
HCN in p-H_2

$v_0 + 8.807$ 2

2,2 7.014
2,1 6.291
2,0 ------
$v_0 + 6.070$
(calc)

2   8.869

7.116 2,2
6.427 2,1
       2,0
6.223
(calc)

$v_0 + 2.936$

1,0 2.720
1,1
$v_0 + 2.116$ 1

2.956
1

2.707 1,0
2.225 1,1

$v_0 + 0.000$ $v_0 + 0.000$
0,0   0

J, M J

$v_1 = 1$

0   0.000   0.000   0,0

J J, M

$v_1 = 0$

$v_{0, pH2} = 3302.989$ cm⁻¹
$v_{0, gas} = 3311.468$ cm⁻¹

Crystal field theory (linear molecule in HCP lattice) *

$$H = H_{r,v} + V_{cry}$$

$$V_{cry} = \boxed{\varepsilon_2} C_{2,0}(\Omega_{HCN}) + \boxed{\varepsilon_3}[C_{3,-3}(\Omega_{HCN}) - C_{3,3}(\Omega_{HCN})]$$

where $C_{l,m}(\Omega) = \left(\dfrac{4\pi}{2l+1}\right)^{1/2} Y_{l,m}(\Omega)$

"Fitting" Results: (10 levels, 9 parameters)

	p-H_2	Gas	
B	1.475(5)	1.478	Identical!
ΔB	-0.005(5)	-0.010	
D	0.0675(5)	2.910×10^{-6}	$\times 20,000!$
ΔD	0.0032(5)	0.025×10^{-6}	
v_0	3302.989(5)	3311.4770	
ε_2	-1.274(5)	-	very large!
$\Delta \varepsilon_2$	-0.193(5)	-	
ε_3	6.850(5)	-	
$\Delta \varepsilon_3$	0.767(5)	-	

NOTE: Above perturbation does not converge for large D! Treatment was modified to incorporate centrifugal distortion after crystal field calculation to avoid this problem.

Perturbation terms determined by T. Momose, unpublished.

Summary

- **AFRL matrix isolation spectroscopy lab back in business (after 5 years!)**

- **Polarization spectroscopy is helpful with reflection configuration**

    1) New insights into annealing process

    2) Powerful assignment tool

- **Despite size, and strong interaction, HCN does rotate in HCP p-H_2**

    1) Large crystal field perturbation (perturbation theory may not be appropriate)

    2) Large effective centrifugal distortion constant, (D), <u>but B unchanged</u>!

    3) Crystal field calculation does not converge properly when D is large

    4) Incorporating D after the crystal field calculation works well

    5) A single o-H_2 inhibits rotation of HCN

- **Other interesting features left out of the talk…**

    1) Rotational excitation lifetime is sensitive to HCN concentration

    2) Strong induced IR activity in H_2 fundamental region

    3) HCN cluster formation

61th International Symposium on Molecular Spectroscopy, Talk RD10, 22 June 2006, The Ohio State University, Columbus, OH
Approved for Public Release; Distribution Unlimited. AAC/PA 06-02-06-271

18